

Short communication

A membraneless single compartment abiotic glucose fuel cell

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HIGHLIGHTS

- Selectively catalyze glucose in the presence of oxygen in abiotic fuel cell.
- Abiotic catalyst Al/Au/ZnO prepared using hydrothermal method.
- Abiotic glucose fuel cell possesses an open-circuit voltage of 840 mV.
- A maximum power density of $16.2 \mu\text{W cm}^{-2}$ at a cell voltage of 495 mV was obtained.

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ABSTRACT

A simple energy harvesting strategy has been developed to selectively catalyze glucose in the presence of oxygen in a glucose/O₂ fuel cell. The anode consists of an abiotic catalyst Al/Au/ZnO, in which ZnO seed layer was deposited on the surface of Al/Au substrate using hydrothermal method. The cathode is constructed from a single rod of platinum with an outer diameter of 500 μm. The abiotic glucose fuel cell was studied in phosphate buffer solution (pH 7.4) containing 5 mM glucose at a temperature of 22 °C. The cell is characterized according to its open-circuit voltage, polarization profile, and power density plot. Under these conditions, the abiotic glucose fuel cell possesses an open-circuit voltage of 840 mV and delivered a maximum power density of $16.2 \mu\text{W cm}^{-2}$ at a cell voltage of 495 mV. These characteristics are comparable to biofuel cell utilizing a much more complex system design. Such low-cost lightweight abiotic catalyzed glucose fuel cells have a great promise to be optimized, miniaturized to power bio-implantable devices.

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1. Introduction

Bio-implantable devices, such as implantable glucose biosensors, require a power source, which may be provided by charging of a battery. The two basic and most immediate challenges facing bio-implantable devices include (1) a high desire that bio-implantable devices are self-powered without using a battery and (2) the power source that can drive bio-implantable devices must not add much weight to the bio-implantable device. Therefore, it is important to exploit innovative nanotechnologies that harvest energy from the environment for self-powering these bio-implantable devices. Self-powering bio-implantable devices have an enormous potential to improve individual's well-being. A key advantage of self-powered bio-implantable devices is that they usually operate at extremely low power (nW to μW) [1]. As a result, the biochemical energy harvested from within the human body is sufficient to power these

systems. By harvesting a small fraction of this energy into electricity, sufficient energy can be generated for self-powering wireless bio-implantable devices by harvesting energy directly from the biological fluid without using external battery sources. The realization of glucose as an ideal fuel source for bio-implantable devices such as miniaturized biosensors [2], microactuators [3], and pacemakers [4] has received significant attention in the development and characterization of enzymatic biofuel cells which convert the biochemical energy from glucose into electrical energy [5].

In enzymatic biofuel cells, glucose is oxidized at the anode by glucose oxidase and oxygen is reduced at the cathode by laccase or bilirubin oxidase [6]. In non-compartmentalized enzymatic biofuel cells, the presence of oxygen and glucose mixture results in the reduction at the cathode as well as at the anode, which results in a decrease in the overall power output of such a device [7]. Moreover, there are significant problems with extending the lifetime and durability of these biocatalysts and hence further decreasing the efficiency of enzymatic biofuel cells since these enzymes have different optimum operating pH and temperature conditions and may require the use of electron transfer mediators [8]. To overcome

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these problems several approaches have been considered such as the use of enzyme with reconstructed active centers that are less sensitive to oxygen [9], inorganic materials such as osmium containing redox polymers [10,11] and carbon nanotubes [4,12–15] that act as mediators or the combination of inorganic mediators and biocatalyst [16] in order to facilitate the efficient electron transfer between the anode and cathode. Glucose dehydrogenase is frequently used in enzyme-biofuel cells and requires the immobilization of NAD⁺ cofactor. The co-immobilization of NAD⁺ cofactor requires the utilization of complex procedures [17], which limits its application in the bio-implantable devices [18]. Thus, in order to achieve kinetically preferential electron transfer, O₂ dependent and NAD⁺ dependent enzymatic biofuel cells must employ complex multimolecular arrangement in the fabrication of the cells. These multimolecular ensembles are not readily adaptable for batch fabrication and are insufficient to provide the long-term power that bio-implantable devices require. Although abiotic glucose fuel cells exhibit higher stability and lifetime than enzymatic biofuel cells, abiotic glucose fuel cells have received very little attention for being used as a potential power source for bio-implantable devices. Generally, abiotic glucose fuel cell are used to convert the chemical energy of glucose and oxygen in biological fluid into electricity using noble metal as the catalyst to abiotically catalyzed glucose because they are inert and biocompatible [19]. In this contribution, we refocus the attention on the development of a simple approach to harvest the excellent electrochemical properties of the Al, Au, and ZnO by combining them via sputtering and hydrothermal methods to fabricate an abiotic glucose/oxygen fuel cell. We utilized the Al/Au/ZnO as the anode and platinum as the cathode material to selectively catalyze glucose oxidation and oxygen reduction in the presence of oxygen.

2. Experimental methods

2.1. Materials

Pure Aluminum foil (99.999%, 250 µm thick) was purchased from Alfa Aesar. Zinc chloride (99.99%), triethenamine (TEA, 99.99%), and all chemical reagents were purchased from Sigma-Aldrich and all supplementary chemicals were of analytical grades and used without further purification. All solutions were prepared with 18.2 MΩ cm Milli-Q water.

2.2. Fabrication

2.2.1. Al/Au/ZnO anode fabrication and Pt cathode

Fig. 1 illustrates the anode fabrication steps for glucose oxidation. Briefly, rectangular (6 mm × 5 mm) strips of pure Al foils were used as substrates and were cleaned to remove contaminants by standard cleanroom procedures prior to use. Thin layers of gold (40 nm) were sputtered onto the surface of the aluminum substrate using the magnetron sputtering process. ZnO seed layers were coated on the Al/Au sputtered substrate by a simple sol–gel process [20] under mild conditions. The ZnO precursors were prepared using zinc chloride and propanol. Briefly, the reaction solution for ZnO seed layer fabrication was prepared by mixing appropriate quantities of propanol and 0.4 M zinc chloride solution under constant stirring at 75 °C. Equimolar of triethenamine was added dropwise to stabilize the precursor solution and produce a final 0.1 M homogeneous ZnO nanosol. The ZnO nanosol was covered and maintained under constant stirring at 85 °C until a homogeneous solution was observed. The reaction mixture was aged at room temperature until the desired consistency was obtained. The Al/Au/ZnO seed layers were established by coating the Al/Au substrate with the ZnO nanosol using dip-coating method followed by

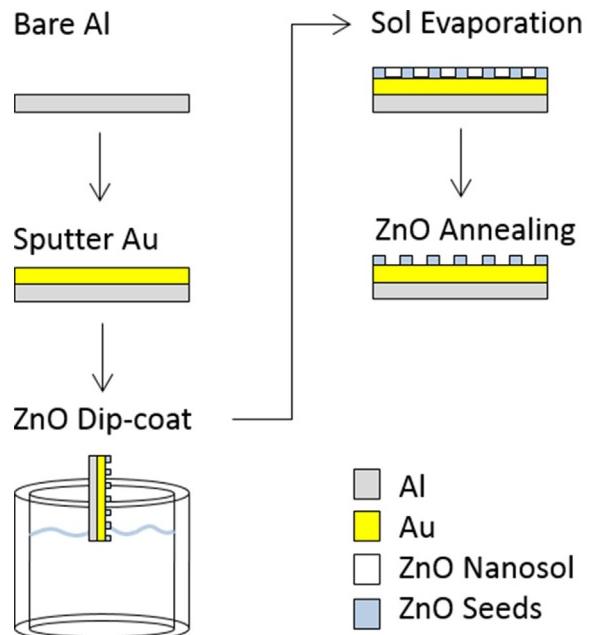


Fig. 1. Cross-section process flow diagram of the fabrication process used in the design of the Al/Au/ZnO anode.

natural solvent evaporation to form a thick layer of seeds. Between coatings, the substrate was annealed at 150 °C for 1 h to ensure nanoparticles adhesion to the substrate surface. The dip-coating and annealing process was repeated until a thick, uniform seed layer was obtained on the surface of the electrode. Subsequently, the Al/Au/ZnO substrates were repeatedly rinsed using deionized water to remove unbound salt and dried at 30 °C in a convection oven overnight. The cathode for oxygen reduction was achieved by utilizing platinum rod ($\phi = 500 \mu\text{m}$) since platinum has been shown to exhibit the highest oxygen reduction potential when compared to palladium, gold and silver in phosphate buffer pH = 7 [21]. The morphology and structural characteristics of the as-fabricated, annealed Al/Au/ZnO were observed by means of scanning electron microscopy (JEOL JSM-5600 SEM).

2.3. Experimental setup

2.3.1. Glucose fuel cell setup and measurements

The abiotic glucose fuel cell was built using the as-fabricated Al/Au/ZnO as the anode and a platinum rod as the cathode positioned 20 mm apart in the cell. **Fig. 2** shows the schematic diagram of the experiment setup. All experiments were performed at physiological glucose and pH levels (5.0 mM glucose in 0.1 M phosphate buffer solution (pH = 7.4)) at 22 °C. The Al/Au/ZnO selectively catalyzes glucose oxidation in the presence of oxygen and the highly specific platinum catalyzes oxygen reduction reaction at the cathode, thereby enabling the use of a membraneless single compartment design for testing. The current–voltage outputs of the cell were obtained under various loads with 5 mM glucose in phosphate buffer. The load was connected directly in parallel with the glucose fuel cell. Fluke 87V True RMS multimeter was used to capture the glucose fuel cell voltage and current readings.

3. Results and discussion

Recently, zinc oxide nanostructures have received significant attention in the construction of sensors [22] and piezoelectric

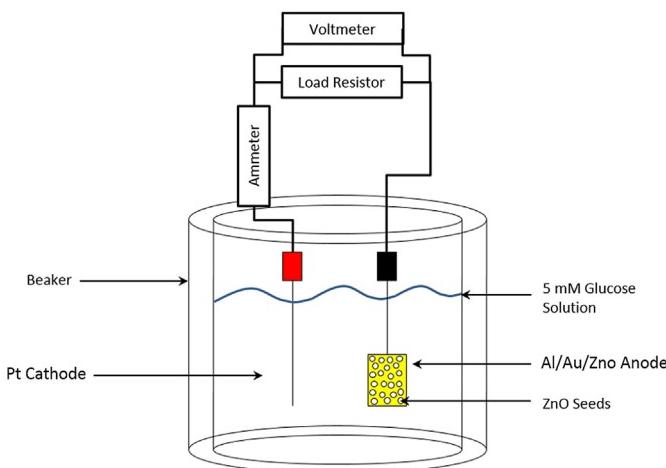


Fig. 2. Experimental set-up for the glucose fuel cell characterization.

generators [23]; however their potential has yet to be explored for abiotic glucose fuel cell applications. Therefore, ZnO seed layers were prepared via sol–gel and dip-coating techniques, and the Al/Au/ZnO substrate was examined by SEM. Fig. 3 shows the SEM images of the as-fabricated Al/Au/ZnO substrate before and after dip-coating with ZnO nanosol. The representative morphology confirms that before dip-coating of ZnO seed layers, the Al/Au substrate was observed to have homogeneous surfaces, whereas after dip-coating in the ZnO nanosol and annealing at 150 °C resulted in nanostructured surface. The nanostructures adopted an irregular morphology with different sized particles (nm range) and formed agglomerates due to the synthesis condition of depositing ZnO seed layers on the surface of Al/Au substrate.

Fig. 4 depicts the cyclic voltammograms (CVs) of the Al/Au/ZnO electrode measured in air-saturated phosphate buffer solution without glucose (purple curve (in the web version)), with 5 mM glucose (blue curve), 10 mM glucose (red curve) and 25 mM glucose (green), respectively. The addition of glucose resulted in the formation of greater oxidation currents. The electrochemical oxidation/reduction of ZnO resulted in redox peaks with anodic and cathodic peak potentials of 1.60 V and 0.51 V in phosphate buffer solution (purple curve). This electrochemical reaction of ZnO appears to be irreversible since the half-wave potential is 1.05 V and the limiting oxidation current is 677.5 μA. It has been reported that the electrochemical redox reaction of ZnO structures in batteries is not reversible [24]. The peak potentials and peak currents of the

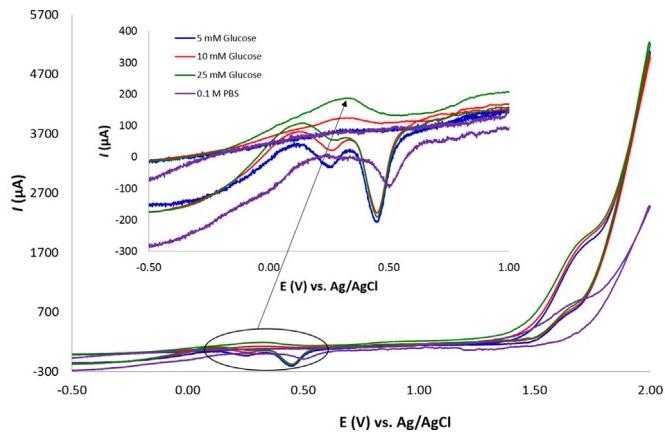


Fig. 4. Cyclic voltammograms (CVs) of the Al/Au/ZnO electrode in air-saturated phosphate buffer solution (pH 7.4) without glucose, with 5 mM, 10 mM, and 25 mM glucose. Scan rate; 20 mV s⁻¹.

redox reaction of the ZnO nanostructures with and without glucose were very similar. The expected reduction of water was not observed in the CV possibly due to the electrocatalytic activity of ZnO. However, the anodic current produced by the Al/Au/ZnO electrode in the presence of glucose corresponds to glucose oxidation at potentials more positive than 338 mV vs Ag/AgCl, while the cathodic current for the oxygen reduction was observed at 445 mV vs Ag/AgCl, thus allowing potential difference of ca. 107 mV between the anodic and cathodic reactions. The increase in oxidation currents corresponds with the glucose oxidation under ZnO electrocatalysis.

The working principle of the abiotic glucose fuel cell is based on the electrochemical property of the Al/Au/ZnO–Pt to oxidize glucose in the presence of oxygen to gluconic acid and reduce oxygen to water, thereby resulting in the generation of electrons (Scheme 1). In addition, the electrons in the valence band of ZnO acts as charge carriers causing ZnO to exhibit n-type conductivity. Hence, the Zinc in ZnO is acts as a deep acceptor, whereas oxygen acts as a deep donor. In the present experiment, ZnO nanostructures can electronically mediate the glucose oxidation indicating that the Al/Au/ZnO had good catalytic performance. During the electrochemical reaction, the relatively dilute potassium phosphate is reacting with ZnO by donating its electrons present in its phosphate group to zinc in ZnO. The generated electrons flow from the anode to the cathode through the external load circuit. This flow of electron process results in a d.c. power source. The highest theoretical voltage that may be obtained from abiotic glucose fuel cell is dictated by thermodynamics and is 1.3 V [21]. Fig. 5 shows the current voltage behavior of the glucose fuel cell at

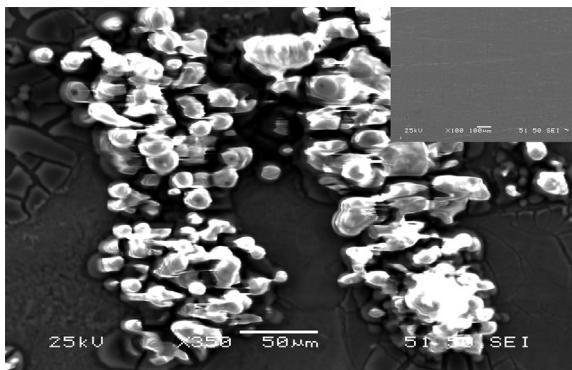
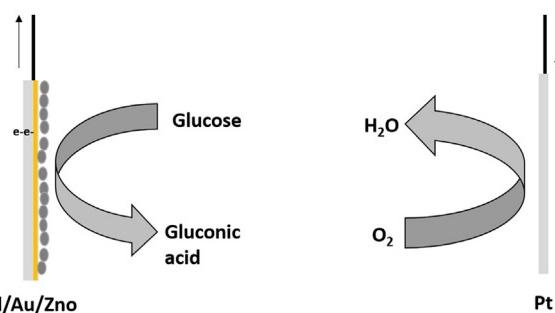


Fig. 3. SEM micrograph of the hydrothermally deposited ZnO nanoparticles on Al/Au. Insert: SEM image of the Al/Au.



Scheme 1. Schematic illustration of glucose oxidation mechanism of Al/Au/ZnO electrodes.

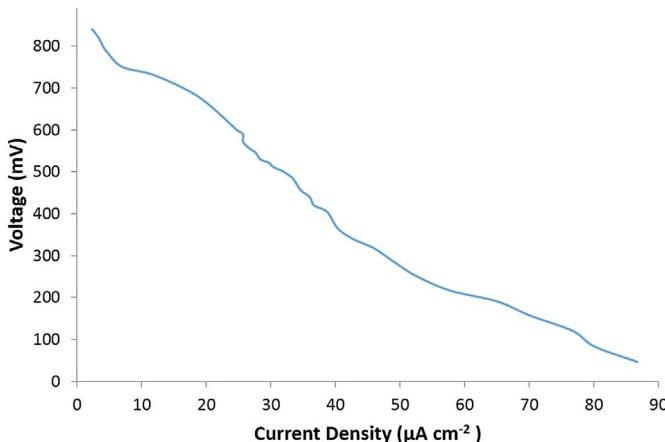


Fig. 5. Current–voltage polarization curve of the glucose fuel cell at different external loads in air-saturated phosphate buffer (pH 7.4) containing 5 mM glucose.

different external loads in 5 mM glucose in phosphate buffer solution saturated with air. 5 mM glucose in buffered solution (pH 7.4) was chosen because blood glucose concentration fluctuates between 4 and 6 mM and has a pH of 7.35–7.45 [11]. The open circuit voltage and short circuit current of the fuel cell was 880 mV and 28 μA , respectively. In addition, the Al/Au/ZnO fuel cell operates without the use of a membrane/stack material to spatially separate the electrodes within a single compartment containing glucose and oxygen. This characteristic is especially unique with respect to abiotic fuel cells as most operate using a membrane in order to isolate the anode and cathode during fuel cell operation. However, the lower open circuit potential observed is due to the occurrence of mixed potentials at both anode and cathode as a result of small amount of glucose and oxygen reacting at the same electrode, which is consistent with abiotic fuel cells [25]. The Al/Au/ZnO shows high degree of selectively oxidizing glucose in the presence of oxygen. To obtain this theoretical voltage, optimization of various factors is required. However, the most important factor is the electrocatalytic surface interactions. The output of the Al/Au/ZnO–Pt fuel could be improved by growing a homogenous layer of ZnO on the Al/Au substrate in the future, so that higher electrocatalytic surface area can be realized in order to obtain a greater voltage

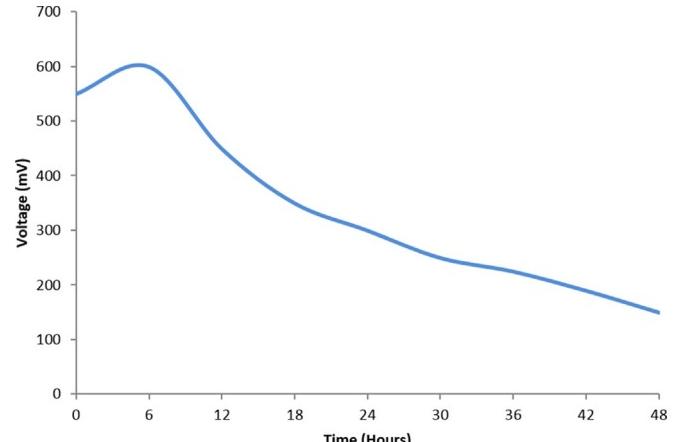


Fig. 7. Voltage generated by cell operated on a 54 k Ω resistance as a function of time.

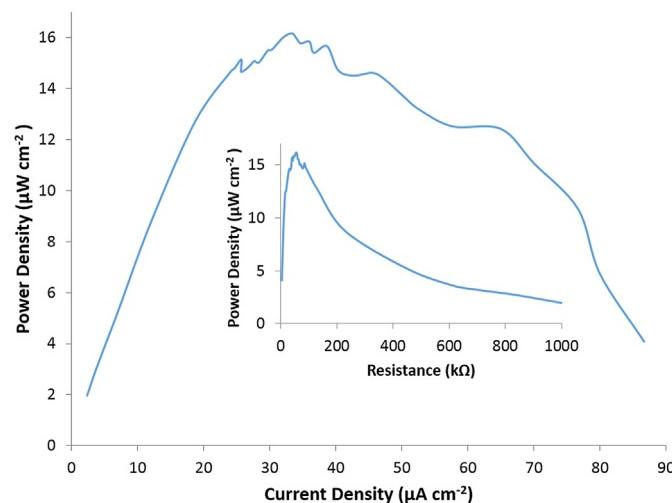


Fig. 6. Power versus current density at different loads of the Al/Au/ZnO–Pt glucose fuel cell. Insert: Power generated on a variable-load resistance.

from the catalysis of glucose [26]. The power of the cell at different loads is shown in Fig. 6. The power density of the Al/Au/ZnO–Pt fuel cell depends on load matching and was found to have a maximum at 54 k Ω with a corresponding power density of 16.2 $\mu\text{W cm}^{-2}$ and a current density of 111.1 $\mu\text{A cm}^{-2}$, which is substantially higher than reported values for a stacked electrode, enzyme-free glucose fuel cell [27] and PQQ-dependent glucose dehydrogenase biofuel cell [15]. In addition, multiple Al/Au/ZnO–Pt fuel cells could potentially be connected in series and/or parallel to further boost the power output.

Fig. 7 shows the stability curve of cell operating continuously under 54 k Ω load in air-saturated 5 mM glucose. The cell demonstrated stable electrical power output over a long period of time (ca. 9 h) followed by a gradual decay in activity, thus confirming the stability of the abiotic catalyst systems. In comparison to enzymatic glucose biofuel cells, one of the major limitations is the performance deteriorate over time as a result of enzymes degradation [28], which renders their application in a long-term bio-implantable device difficult as seen in the case of glucose oxidase and glucose dehydrogenase based fuel cells [7,15]. Therefore, the Al/Au/ZnO–Pt fuel cell which harvests the biochemical energy of glucose is an attractive alternative to enzymatic glucose biofuel cells for its increased power output and lifetime. The reported fuel cell has the benefit of high power density and potentially operating over longer time periods because the lifetime is only limited by the degradation of the device, which with the advancement in technology can be engineered to be durable.

4. Conclusion

Developing innovative nanotechnologies that harvest energy from our personal environment for self-powering bio-implantable devices is highly desirable for long-term bio-implantable devices. Herein, an Al/Au/ZnO abiotic catalyst was fabricated by hydrothermal and dip-coating techniques for the development of an abiotically catalyzed glucose fuel cell that may enable self-powering of bio-implantable devices. The characterization of the Al/Au/ZnO anode was revealed by the formation of ZnO nanostructures on the surface of the Al/Au substrate having excellent glucose catalysis capability. The Al/Au/ZnO–Pt glucose fuel cell was demonstrated to harvest the biochemical energy from glucose in the presence of oxygen. A peak power density of 16.2 $\mu\text{W cm}^{-2}$ and a current density of 111.1 $\mu\text{A cm}^{-2}$ was obtained. This is an improvement over the current abiotic fuel cell technology that utilizes membrane/stack design scheme to achieve glucose and

oxygen separation by decreasing the occurrence of the oxidation of glucose and reduction of oxygen at the same electrode. Thus, the present contribution provides a platform to use Al/Au/ZnO nanostructured electrode to formulate an efficient membraneless single compartment abiotic glucose fuel cell with stable electrical power over a long period of time. The fabricated abiotic fuel cell could be broadly exploited with more wide application for self-powering bio-implantable devices. Future work will involve chromatographic analysis of the species in solution to confirm the reaction products, reaction mechanism and the limiting reagents, if any.

References

- [1] J. Colomer-Farrarons, P. Miribel-Català, *New Perspectives in Biosensors Technology and Applications*, InTech, 2011, pp. 373–400.
- [2] E. Katz, A.F. Bückmann, I. Willner, *J. Am. Chem. Soc.* 123 (43) (2001) 10752–10753.
- [3] Y. Tanaka, K. Morishima, T. Shimizu, A. Kikuchi, M. Yamato, T. Okanobe, T. Kitamori, *Lab. Chip* 6 (2) (2006) 230–235.
- [4] K. MacVittie, J. Halámková, L. Halámková, M. Southcott, W.D. Jemison, R. Lobel, E. Katz, *Energy Environ. Sci.* 6 (1) (2013) 81–86.
- [5] S. Vaddiraju, I. Tomazos, D.J. Burgess, F.C. Jain, F. Papadimitrakopolous, *Biosens. Bioelectron.* 25 (7) (2010) 1553–1565.
- [6] H. Aurélien, S. Karine, T. Sophie, K. Boniface, *Biofuel's Eng. Process Technol.* (2011) 467–492.
- [7] E. Katz, I. Willner, A.B. Kotlyar, *J. Electroanal. Chem.* 479 (1) (1999) 64–68.
- [8] F. Davis, S.P.J. Higson, *Biosens. Bioelectron.* 22 (7) (2007) 1224–1235.
- [9] M.H. Osman, A.A. Shah, F.C. Walsh, *Biosens. Bioelectron.* 26 (7) (2011) 3087–3102.
- [10] F. Barrièrea, Y. Ferryb, D. Rochefortc, D. Leech, *Electrochem. Commun.* 6 (3) (2004) 237–241.
- [11] A. Heller, *Phys. Chem. Chem. Phys.* 6 (2) (2004) 209–216.
- [12] A. Zebda, C. Gondran, A. Le Goff, M. Holzinger, P. Cinquin, S. Cosnier, *Nat. Commun.* 2 (370) (2011).
- [13] M. Holzinger, A. Le Goff, S. Cosnier, *Electrochim. Acta* 82 (2012) 179.
- [14] M. Rasmussen, R.E. Ritzmann, I. Lee, A.J. Pollack, D. Scherson, *J. Am. Chem. Soc.* 134 (2012) 1458–1460.
- [15] L. Halámková, J. Halámek, V. Bocharova, A. Szczupak, L. Alfanta, E. Katz, *J. Am. Chem. Soc.* 134 (2012) 5040–5043.
- [16] G. Slaughter, K. Amoah, *J. Biosens. Bioelectron.* 3 (4) (2012).
- [17] M. Zayats, E. Katz, I. Willner, *J. Am. Chem. Soc.* 124 (2002) 14724–14735.
- [18] C.W.N. Villarrubia, R.A. Rincon, V.K. Radhakrishnan, V. Davis, P. Atanassov, *ACS Appl. Mater. Interfaces* 3 (2011) 2402–2409.
- [19] A.E. Franks, K.P. Nevin, *Energies* 3 (2010) 899–919.
- [20] R. Wang, J.H. Xin, X.M. Tao, W.A. Daoud, *Chem. Phys. Lett.* 398 (1) (2004) 250–255.
- [21] S. Kerzenmacher, J. Ducrée, R. Zengerle, F. von Stetten, *J. Power Sources* 182 (1) (2008) 1–17.
- [22] M. Yin, M. Liu, S. Liu, *Sens. Actuators B* (2013) 735–742.
- [23] Z.L. Wang, J. Song, *Science* 312 (5771) (2006) 242–246.
- [24] X.-M. Zhu, H.-X. Yang, X.-P. Ai, J.-X. Yu, Y.-L. Cao, *J. Appl. Electrochem.* 33 (2004) 607.
- [25] A. Kloke, B. Biller, U. Kräling, S. Kerzenmacher, R. Zengerle, F. von Stetten, *Fuel Cells* 11 (2) (2011) 316–326.
- [26] M. Tominaga, T. Shimazoe, M. Nagashima, I. Taniguchi, *Electrochim. Commun.* 7 (2) (2005) 189–193.
- [27] V. Oncescu, D. Erickson, *J. Power Sources* 196 (2011) 9169–9175.
- [28] Y. Yan, W. Zheng, L. Su, L. Mao, *Adv. Mater.* 18 (19) (2006) 2639–2643.